THE CATALYTIC HYDROGENATION OF MULTI-RING AROMATIC COAL TAR CONSTITUENTS

Wendell H. Wiser, Surjit Singh,
S. A. Qader, and George R. Hill

Department of Mineral Engineering
University of Utah, Salt Lake City, Utah   84112

Bituminous coal is understood to consist primarily of fused ring structures joined together by various types of linkages to form an extensive network. These ring structures are quite highly aromatic, although considerable quantities of hydro-aromatic configurations are also present. The size of these structures may vary from one to several rings, with an average-sized configuration containing three or four rings.

As one attempts to convert coal to useful liquid materials, it seems desirable to obtain high yields of benzene and its derivatives. These compounds have wide applicability as additives in gasoline to improve the octane rating, as raw materials for the manufacture of conventional explosives, as solvents and chemicals, etc. The higher members of the aromatic homologous series are solids at room temperature. (The melting point of naphthalene, a two-ring structure, is 80°C.)

In the course of coal pyrolysis, a single-ring aromatic constituent existing in the lattice structure may possibly be liberated by rupture of the bond(s) joining it to the structure, followed by stabilization of the fragment thus produced. Similarly, higher members of the aromatic homologous fused series may be produced. These products may then be liberated as volatile products as determined by their respective vapor pressures.

While aromatic-type bonds are not expected to be thermally ruptured to any significant extent in this temperature range, the single carbon-carbon bonds within the hydroaromatic structures may be ruptured. This could lead to ring opening of saturated portions of the hydroaromatic structure, followed by cracking of the side chains thus produced, yielding gases and lower aromatics. It is probable that some of the benzene and its derivatives obtained in coal pyrolysis is produced in this manner.

These processes are greatly assisted by the presence of an agent which can produce atoms or small radicals to stabilize the thermally-produced fragments. Hence, dissolution in an appropriate solvent (e.g., tetralin) produces larger quantities of lower-boiling aromatic materials. Hydrogenation in the presence of an appropriate catalyst yields yet larger quantities of lower-boiling constituents.

The production of benzene and its derivatives may be increased by hydrogenation and hydrocracking of higher members of the aromatic series. For members of the series consisting of three rings or more, two possible approaches may exist. The first approach would consist of hydrogenation of a ring at the end of the cluster, followed by ring opening and cracking to produce a derivative of the next lower member of the aromatic series. This procedure could be repeated, yielding ultimately one molecule of benzene or a benzene derivative for each aromatic cluster thus utilized. The second approach may be the hydrogenation of a ring within the cluster other than an end ring, followed by cracking of this ring to yield two aromatic fragments. Completion of this procedure would yield at least two molecules of benzene or its derivatives for each cluster thus utilized.

The present paper describes initial investigation of these possibilities. In an effort to gain understanding of the basic principles involved, the study was initiated

using pure compounds. The first compound investigated was anthracene, a fused, linear, three-ringed compound. The catalytic hydrocracking studies were then extended to 9,10-dihydroanthracene.

Experimental Procedure

The equipment consisted of an autoclave of one-liter capacity, equipped with a variable speed magnetic stirrer, a pressure gauge, and a thermocouple well. Auxiliary to the autoclave were a temperature recorder to follow the rate of heating, rheostats to assist in obtaining a smooth heating curve, and a temperature controller capable of maintaining constant temperature within $\pm 3°C$.

The hydrogenation experiments were performed using 25 grams of anthracene of 98% purity, mixed with 2.5 grams of catalyst (nickel tungsten sulfide pellets of 1/8-inch diameter). The system was evacuated and then filled with hydrogen to a predetermined cold pressure such that the operating pressure at the temperature of the experiment would be 1500 p.s.i. Approximately 20 minutes were required to bring the system to operating temperature. Solid samples from the reaction products were dissolved in trichloroethylene and analyzed by means of a flame-ionization chromatograph, with an Apiezon-L separation column. Liquids and gases were analyzed by means of the gas chromatograph.

Studies concerning the continued reactions of the 9,10-dihydroanthracene at 510°C were performed using 25 grams of 9,10-dihydroanthracene of 95% purity, mixed with 2.5 grams of catalyst (Kaolin pellets of 1/8-inch diameter or fluid zeolite cracking catalyst). The techniques for hydrogenation and product analyses were similar to those described above.

Results and Discussion

Typical curves from this study showing the rate of disappearance of anthracene during catalytic hydrogenation at various temperatures ranging from 220° to 435°C are shown in Figure 1. These data are presented as weight percent anthracene in the product as a function of time.

Figure 2 shows four chromatograms illustrating the progress of the reactions at 390°C. At 35 minutes, a considerable amount of hydrogenation to 9,10-dihydroanthracene had occurred, followed by some formation of 1,2,3,4-tetrahydroanthracene. At 60 minutes, hydrogenation of anthracene was nearly complete and a considerable amount of the 1,2,3,4,5,6,7,8-octahydro-derivative had been formed. Finally, at 240 minutes, the anthracene had disappeared, together with most of the 9,10-derivative, and ring opening and/or cracking of other anthracene derivatives to yield naphthalene derivatives was becoming significant.

Figure 3 shows four chromatograms which illustrate the progress of the hydrogenation reactions at comparable times as a function of temperature. At 250°C and 240 minutes, most of the anthracene had been hydrogenated, with appreciable quantities of 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene present in the system. Products representing higher stages of hydrogenation were not detected and no cracking was observed to occur. At 300°C and 200 minutes, more of the anthracene had been hydrogenated to the dihydro- and tetrahydro-derivatives, but there was still no evidence of higher stages of hydrogenation, or cracking to naphthalene derivatives. At 390°C and 240 minutes, essentially all of the anthracene had been hydrogenated, with rather small amounts of 9,10- and large amounts of 1,2,3,4-derivatives of anthracene present, but with an appreciable amount of 1,2,3,4,5,6,7,8-octahydroanthracene now present. Naphthalene derivatives, products of the hydrocracking of one or more of the anthracene derivatives, had appeared. At 435°C and 200 minutes, most of the 9,10-dihydroanthracene had been further hydrogenated, with a large quantity of the

octahydroanthracene present, but also with considerable amounts of naphthalene deri-
vatives present. In addition, significant quantities of benzene derivatives were
now observed. They were apparently formed by further hydrogenation and cracking of
the naphthalene derivatives, or perhaps of the remnant of the 1,2,3,4,5,6,7,8-
octahydroanthracene.

Figure 4 shows the rate of production of 9,10-dihydroanthracene during catalytic
hydrogenation of anthracene. The data indicate that this is the first stable com-
pound formed. At 220°C, yields of nearly 80% of this product, by weight, were
obtained. As the temperature increased, the maximum quantity of this compound in
the system decreased due to the continued hydrogenation in other positions on the
molecule. At temperatures of 345°C and higher, the yield of 9,10-dihydroanthracene
reached a maximum, then decreased at longer times due to continuing hydrogenation.

Figure 5 shows the rate of formation of 1,2,3,4-tetrahydroanthracene. It is observed
that at temperatures of 250°C and lower, the yields of this product continued to
approach a maximum value at long times and did not pass through a maximum. The
data indicated only traces of products representing further stages of the hydrogena-
tion process. At higher temperatures, the yields of 1,2,3,4-tetrahydroanthracene
reached a maximum value for each temperature, then diminished due to continuing
hydrogenation.

Figure 6 shows the rate of formation of 1,2,3,4,5,6,7,8-octahydroanthracene as a
continuation of the process of catalytic hydrogenation of anthracene. Since only
traces of this compound were formed at 250°C and lower, these temperatures are not
represented. At 345° and 390°C, the quantities of this compound continued to
increase with time, the data indicating only small quantities of further reaction
products. At 435°C, a maximum quantity of 1,2,3,4,5,6,7,8-octahydroanthracene was
observed, followed by a decrease as cracking of the molecule occurred, to yield
naphthalene derivatives. Only small quantities of naphthalene derivatives were
formed below 435°C.

Figure 7 shows the rate of formation of naphthalene and its derivatives. These com-
pounds are apparently formed by opening a saturated ring on the end of the hydro-
aromatic molecule, perhaps followed by cracking of the side chain produced, to yield
gas and a naphthalene derivative. At temperatures above 500°C, this reaction is
appreciable, but cracking of these structures is very limited at lower temperatures.

As the hydrogenation reactions continued, a second saturated ring was apparently
opened, perhaps followed by cracking of the side chains thus produced, yielding gas
and benzene or its derivatives. Figure 8 shows the rate of formation of these com-
pounds. These reactions occurred only at the higher temperatures at longer times.

The curves at 510°C in Figures 7 and 8 were obtained using 9,10-dihydroanthracene
of 95% purity as the raw material, Kaolin catalyst, and hydrogen pressure of 300
p.s.i. The other curves at the lower temperatures in these two figures represent
the continuing hydrogenation of anthracene described above.

An analysis of the data at a particular temperature (e.g., 435°C) reveals that maxi-
mum quantities of the various hydrogenation products appear in the following order:
9,10-dihydroanthracene (about 40 minutes), 1,2,3,4-tetrahydroanthracene (about 100
minutes), and 1,2,3,4,5,6,7,8-octahydroanthracene (about 140 minutes). The appear-
ance of naphthalene derivatives is subsequent to or concurrent with the appearance
of the octahydroanthracene, suggesting that the ring opening reactions to produce
the naphthalene derivatives may occur primarily on the octahydro derivative of anthra-
cene under the conditions of these investigations. This, however, has not been
verified.

Kaolin, which has proven effective as a cracking catalyst, was tried using 9,10-dihydroanthracene as the raw material, a hydrogen pressure of 300 p.s.i., and a temperature of 510°C. The progress of the hydrocracking reactions is readily observed in Figure 9. At 60 minutes, a considerable quantity of 1,2,3,4-tetrahydroanthracene had formed, accompanied by some dehydrogenation to anthracene due to the equilibrium involving these three compounds. At this time, small quantities of naphthalene derivatives had appeared, but only a trace of benzene derivatives. At 120 minutes, the anthracene had essentially disappeared, accompanied by a further reduction in the quantity of 9,10-dihydroanthracene. There was an observable decrease in the quantity of 1,2,3,4-tetrahydroanthracene, accompanied by the production of a considerable quantity of 1,2,3,4,5,6,7,8-octahydroanthracene. The yields of naphthalene derivatives had become significant by this time (approximately 6.5 wt. percent) and small amounts of benzene derivatives had appeared. At 240 minutes, the anthracene derivatives had diminished greatly, accompanied by formation of rather large amounts of naphthalene derivatives (approximately 44 wt. percent) and a significant quantity of benzene derivatives (approximately 18 wt. percent).

The data for the hydrogenation of anthracene, as represented by the rate of disappearance of anthracene in Figure 1, may be analyzed by applying a first-order differential equation. If the average molecular weight of the products of reaction remains essentially constant (a good approximation until cracking becomes significant), weights may be used in the equation.

$$\frac{dx}{dt} = k'(a-x) \qquad (1)$$

where "x" is the weight fraction of anthracene which has reacted at time "t", "a" is the initial weight fraction of the anthracene which may react at infinite time, and "k'" is the reaction velocity constant. Integrating equation 1 and evaluating the constant of integration with $x = 0$ when $t = 0$ yields:

$$\ln \frac{a}{a-x} = k't \qquad (2)$$

A plot of equation 2 is shown in Figure 10, where the reasonably straight lines indicate that the hydrogenation of anthracene at 1500 p.s.i. hydrogenation pressure is first order in the temperature range of 220° to 435°C.

The rate of a chemical reaction is determined by the free energy of activation. The reaction velocity constant may be related to the free energy of activation by the following equation (1):

$$k' = \mathcal{H} \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT} \qquad (3)$$

or, since $\Delta F = \Delta H - T\Delta S$:

$$k' = \mathcal{H} \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad (4)$$

where $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are the free energy, heat, and entropy of activation, respectively, "k" is the Boltzmann constant, "h" is the Planck constant, and $\mathcal{H}$ is a transmission coefficient representing the fraction of activated complexes which leads to formation of products (usually considered equal to one).

Equation 4 may be written in the form:

$$\ln \frac{h}{\mathcal{H}k} \frac{k'}{T} = \frac{-\Delta H^{\ddagger}}{R} \frac{1}{T} + \frac{\Delta S^{\ddagger}}{R} \qquad (5)$$

Figure 11 represents a plot of equation 5 from which is obtained an activation enthalpy of 3.8 kcal/mole and an entropy of activation of -15.5 entropy units. The small activation enthalpy indicates that physical factors rather than chemical reactions control the overall rate of the process. The possibilities include diffusion of the anthracene to the catalyst surface, orientation and adsorption on the catalyst surface, desorption of the reaction products from the catalyst surface, and diffusion of these products away from the surface. This study does not provide information to identify the rate-controlling process.

In the formation of a covalent bond between two atoms, the resonance energy of the electrons involved increases in magnitude as the degree of overlapping of the atomic orbitals involved increases (2). (The word "overlapping" signifies the extent of coincidence of the regions in space in which the orbital wave functions have large values.) This resonance energy in large measure accounts for the energy of the covalent bond. Hence, other factors excluded, shorter bonds between two atoms would possess greater energy than longer bonds between the same two atoms.

If one considers the linear series, benzene (1 ring), naphthalene (2 fused rings), anthracene (3 fused rings), naphthacene (4 fused rings), etc., a very marked and progressive increase in reactivity is noted as the series is ascended (3). Thus, pentacene (5 linear fused rings) is highly reactive and heptacene (7 rings) is so reactive that it is impossible to obtain it in a pure state. This increase in reactivity is accompanied by an increase in tendency to yield addition rather than substitution products. Thus, anthracene is more likely to react by addition than by substitution under mild conditions.

Whereas a conjugated molecule (e.g., the polyenes) manifests alternate longer and shorter bonds, aromatic compounds do not. Hence, in benzene all bonds are equal to about 1.39 Å. Variations in bond distances occur in multiring compounds, but not alternately. Hence, the observed bond distances in the anthracene molecule are as follows (3):
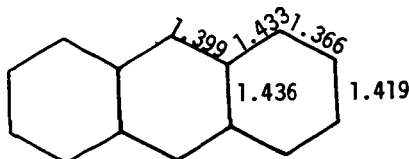
The various positions on the multiring aromatic molecule manifest different degrees of reactivity. Hence, anthracene was observed in this study (as well as by other investigators) to add hydrogen in the 9 and 10 positions to form the dihydride, producing yields of this compound as high as 80% by weight under carefully controlled conditions. As the series is ascended, the stability of the dihydro-derivatives increases notably. Thus, dihydrobenzene is relatively unstable; 1,4-dihydronaphthalene is moderately stable; but 9,10-dihydroanthracene is a stable compound. With some of the higher members of the series, the tendency to form dihydro-derivatives is very marked, such that when heated, part of the compound is decomposed and part converted to the dihydride.

The addition of hydrogen in the 9 and 10 positions of the anthracene molecule (and in comparable positions away from an end ring on the higher aromatic homologues) would alter the aromatic nature of the bonds adjacent to these positions. One might expect a reduction in the resonance energy of the electrons associated with these bonds due to this alteration in aromatic nature, with a resulting weakening and lengthening of the bonds. It would then be theoretically possible to rupture these bonds in preference to other bonds within the fused structure. To date, such a rupture has not been observed to occur. Attempts to catalytically hydrocrack the 9,10-dihydroanthracene resulted in hydrogenation in the 1,2,3,4 positions with an

accompanying shift of hydrogen from the 9 and 10 positions. This shift is probably associated with the change in electron orbitals incident to the removal of the aromaticity of the ring involving the 1,2,3,4 positions.

Acknowledgment

References

1. Glasstone, S., Laidler, K. J., Eyring, H., "Theory of Rate Processes," McGraw-Hill, New York, 1941.

2. Pauling, L., "The Nature of the Chemical Bond," Chap. III, Cornell University Press, Ithaca, New York, 1948.

3. Badger, G. M., "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, Great Britain, 1969.
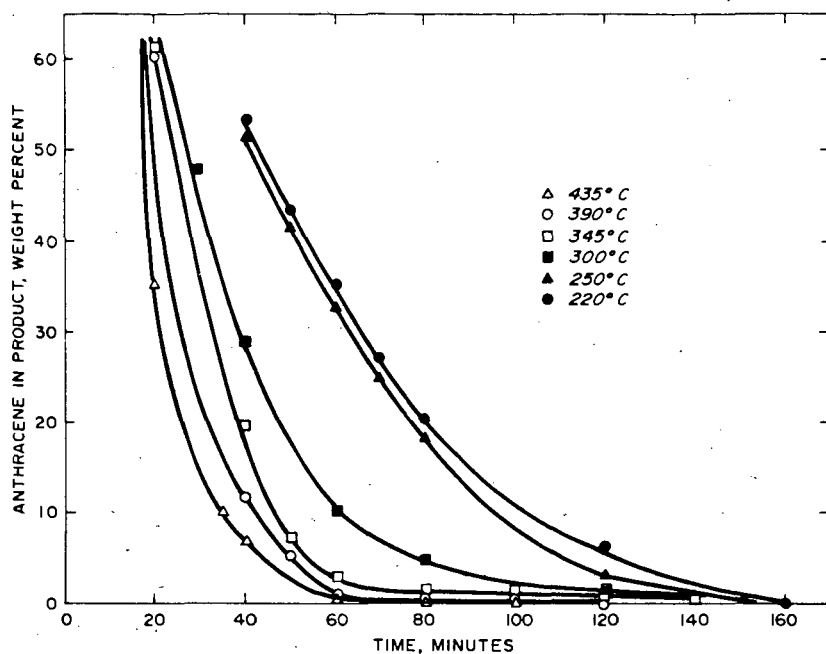
FIGURE 1 RATE OF DISAPPEARANCE OF ANTHRACENE DURING CATALYTIC HYDROGENATION.
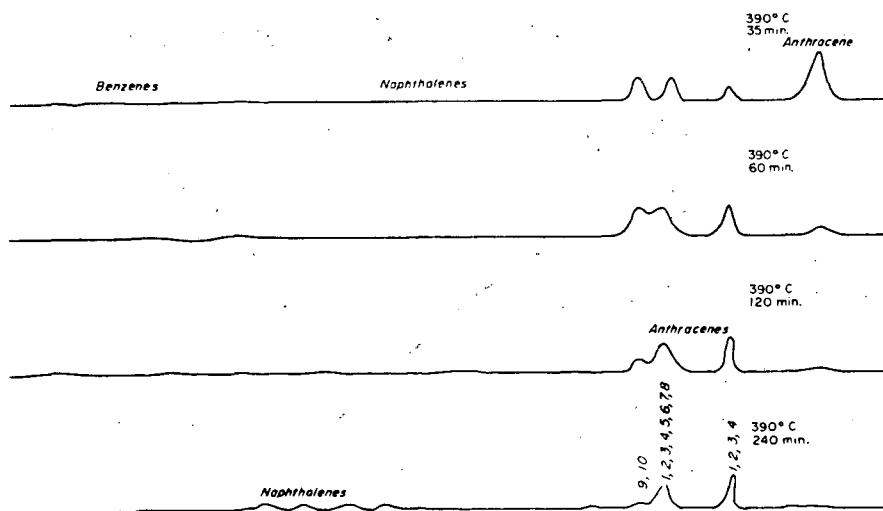
FIGURE 2 CHROMATOGRAMS SHOWING PRODUCT DISTRIBUTION ON HYDROGENATION OF ANTHRACENE AT 390° C, 1500 PSI, Ni - W - S CATALYST.
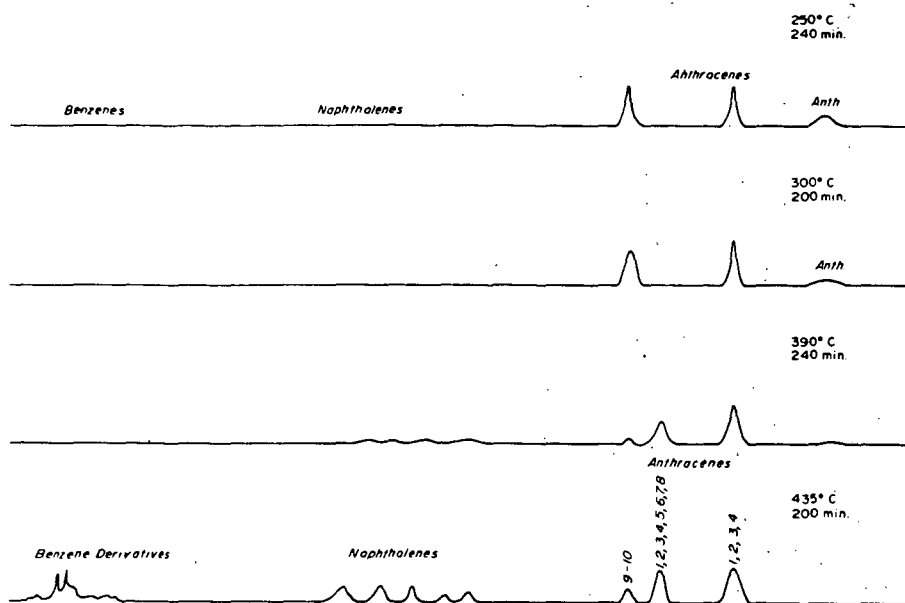
FIGURE 3 CHROMATOGRAMS SHOWING PRODUCT DISTRIBUTION ON HYDROGENATION OF ANTHRACENE AT 250°C TO 435°, 1500 PSI.
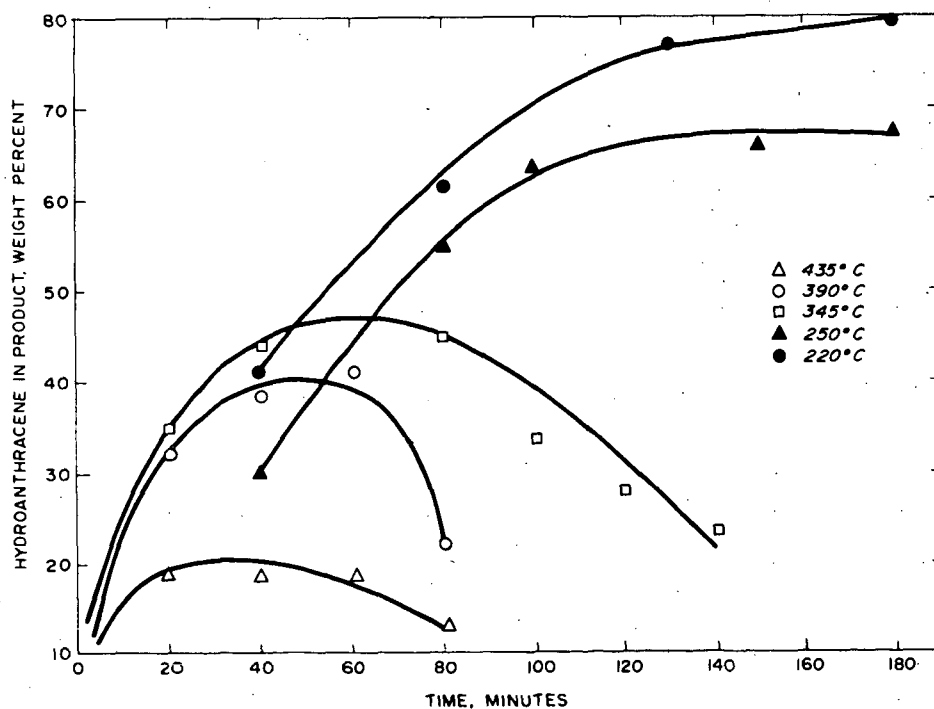
FIGURE 4 RATE OF FORMATION OF 9,10 – DIHYDROANTHRACENE DURING CATALYTIC HYDROGENATION OF ANTHRACENE.
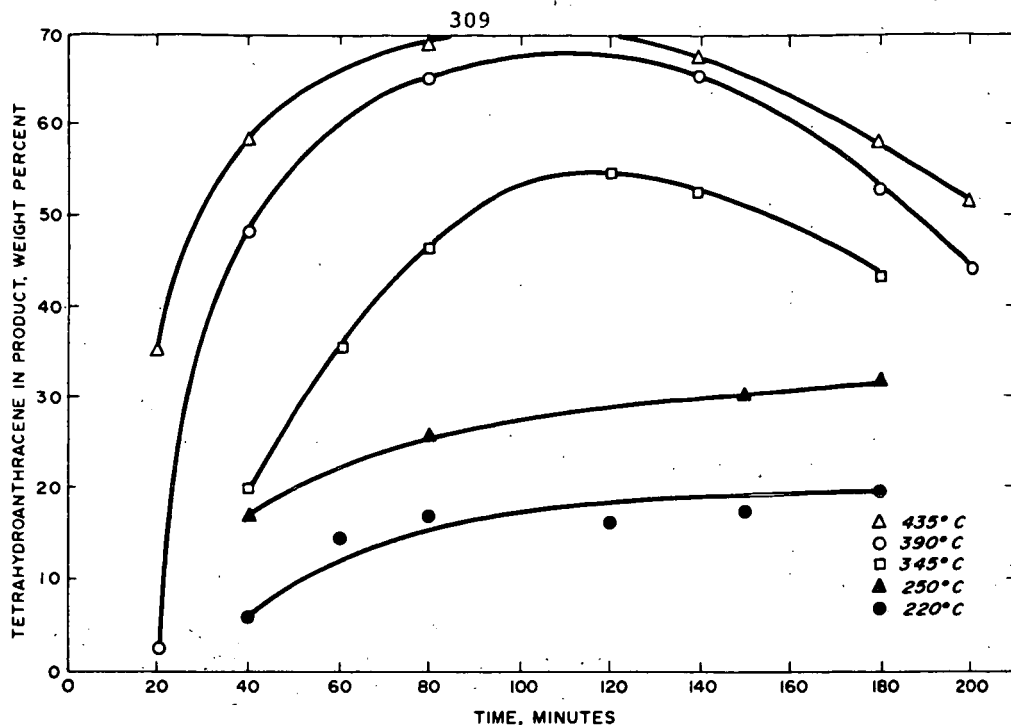
FIGURE 5   RATE OF FORMATION OF 1, 2, 3, 4 - TETRAHYDROANTHRACENE DURING HYDROGENATION OF ANTHRACENE.
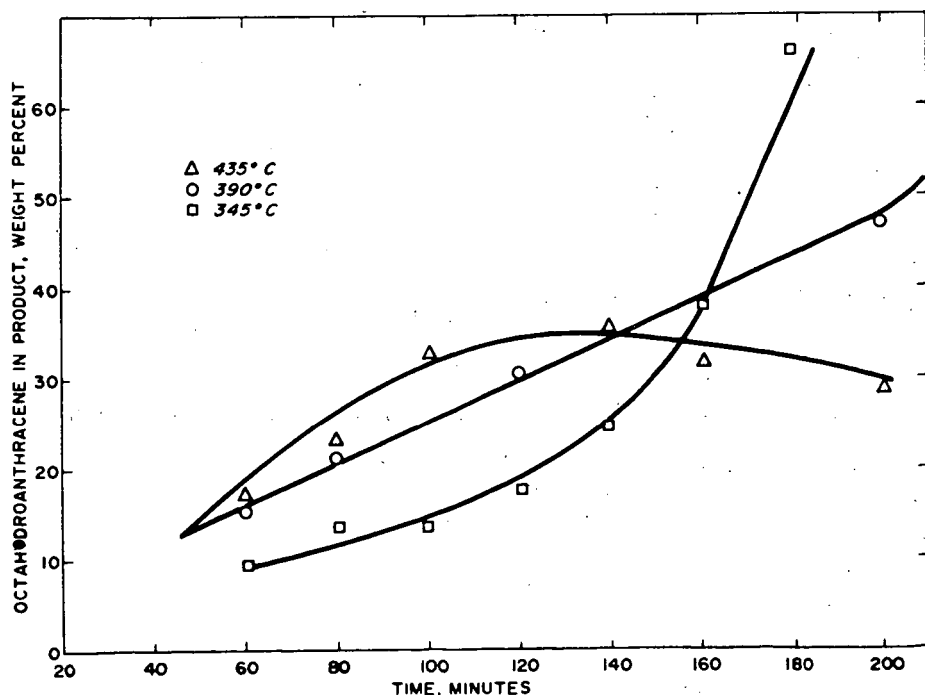
FIGURE 6   RATE OF FORMATION OF 1, 2, 3, 4, 5, 6, 7, 8, - OCTAHYDROANTHRACENE DURING HYDROGENATION OF ANTHRACENE.
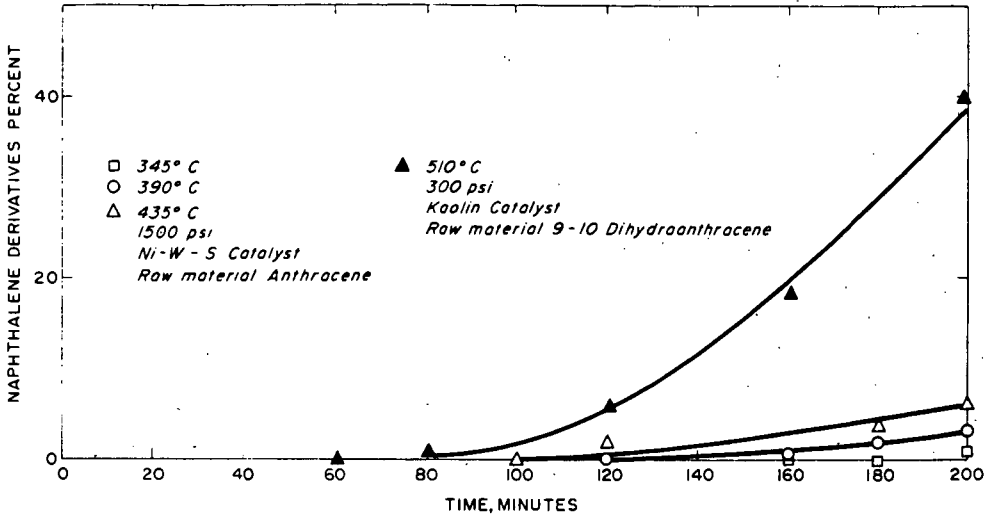
FIGURE 7 RATE OF FORMATION OF NAPHTHALENE DERIVATIVES DURING HYDROGENATION AND HYDROCRACKING.
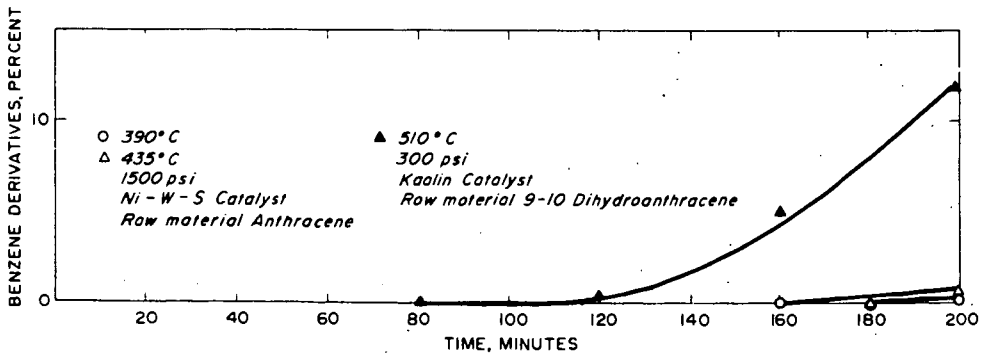
FIGURE 8 RATE OF FORMATION OF BENZENE DERIVATIVES DURING HYDROGENATION AND HYDROCRACKING.
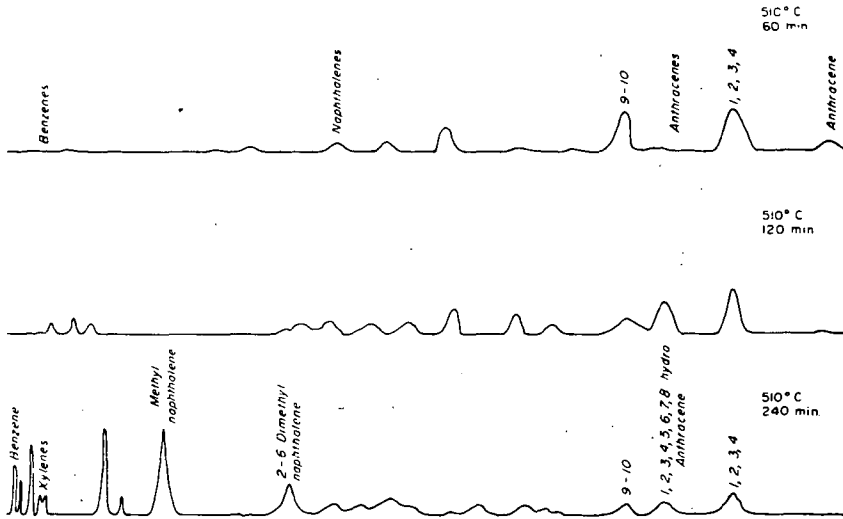
FIGURE 9 CHROMATOGRAMS SHOWING PRODUCT DISTRIBUTION ON CRACKING 9-10 DIHYDROANTHRACENE, 510° C, 300 PSI.
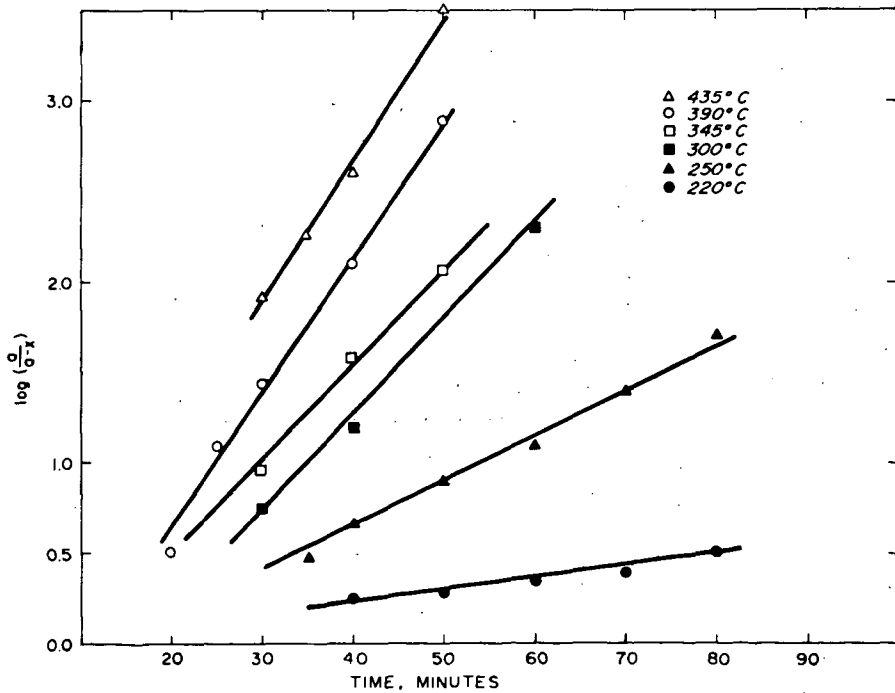

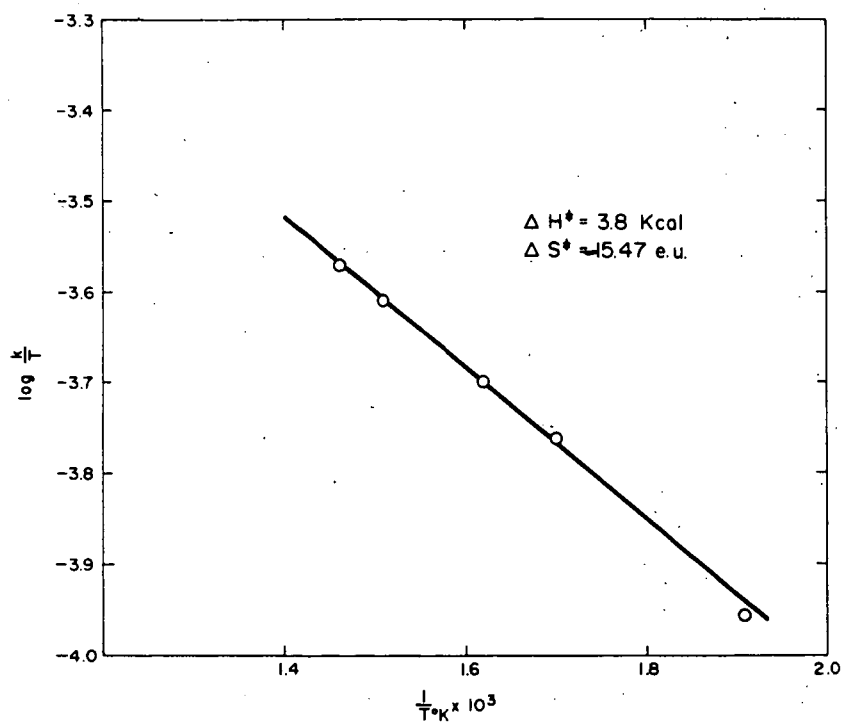FIGURE 10 FIRST-ORDER PLOT FOR ANTHRACENE IN PRODUCT DURING HYDROGENATION OF ANTHRACENE.

FIGURE II   ABSOLUTE REACTION RATE PLOT OF HYDROGENATION OF ANTHRACENE.